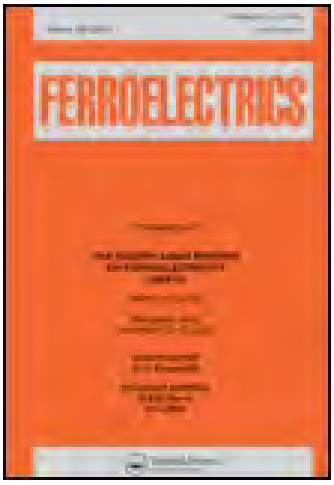

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Tetragonal Tungsten Bronzes in $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$ Microwave Ceramics

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For the first time, the dielectric properties of the 9:1:7 TTB phases $Ba_9M^{2+}Nb_{14}O_{45}$ (M = Co, Mg, Zn) which form in Ba-deficient high-Q perovskite niobates $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$ have been measured in the radio-frequency and microwave range. The low-temperature dielectric relaxation found in $Ba_9M^{2+}Nb_{14}O_{45}$ was shown to give a strong contribution into their microwave dielectric loss. The measured data were used for a simple simulation of the Q-factor of a perovskite-TTB composite. Calculated parameters have been shown to correspond well to the measured data.

Keywords Tetragonal tungsten bronzes; ordered perovskites; dielectric properties; quality factor; composites

1. Introduction

Microwave ceramics based on the complex perovskites $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$ (M = Co, Zn, Mg) have been attracting sustainable interest as the dielectric resonator materials with potentially high quality factor ($Q = 1/\tan\delta$) in the centimeter and millimeter wavelength bands [1–5]. For example, the Q×f product as high as 230 000 GHz at frequencies above 60 GHz has been reported for $Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics [5]. However, microwave dielectric properties of the perovskite niobates to a large extent depend on several competing factors like cation ordering in the B-sublatice, densification of ceramics, microstructural defects, and presence of secondary phases. Moreover, in many cases the latter factor may prevail over other ones resulting in significantly changing microwave characteristics [6]. Main secondary phases which are generally detected in the ceramics $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$ are either layered hexagonal perovskites $Ba_5Nb_4O_{15}$ and $Ba_8M^{2+}Nb_6O_{24}$ or tetragonal tungsten bronzes (TTB) $Ba_9M^{2+}Nb_{14}O_{45}$ [4, 6]. Previously, the presence of the TTB phases in the perovskite matrix $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$ was shown by various authors to accompany declining Q in sintered materials with increasing Ba-deficiency in their compositions [4, 6].

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However, neither properties of the corresponding TTB compounds nor their effect on the multiphase ceramics in the microwave range have previously been reported. In our most recent study we have found low-temperature relaxation of both permittivity (ε) and dielectric loss (tan δ) of near single-phase $Ba_9M^{2+}Nb_{14}O_{45}$ ceramics [7]. Apparently, the observed dielectric relaxation may give strong contribution to the microwave dielectric loss of the perovskite-TTB diphase composites. Therefore, the main goal of this work was to evaluate such a potential contribution deriving from the microstructure of composite ceramics as well as properties of their constituent parts.

2. Experimental Procedure

Ceramic materials with the compositions $Ba(M^{2+}{}_{1/3}Nb_{2/3})O_3$ (perovskite) and $Ba_9M^{2+}Nb_{14}O_{45}$ (TTB) have been produced by the conventional mixed-oxide route. M^{2+} was Co, Mg, and Zn. The starting reagents were extra pure MgO, ZnO, Co_3O_4 (99.95%), Nb_2O_5 (99.9%), and $BaCO_3$ (99.9%). Perovskites have been synthesized by a two-stage process through intermediate synthesis of the columbites $M^{2+}Nb_2O_6$. The calcinations temperatures of the mixtures Co_3O_4-$3Nb_2O_5$, MgO-Nb_2O_5, ZnO-Nb_2O_5 have been chosen as 1150°C, 1200°C, and 1000°C respectively. The soaking time was 4 hours. At the second stage the appropriate ratios of $BaCO_3$ and corresponding columbite were ball milled again, and calcined at 1150°C–1250°C for another 4 hours. The sintering was performed in air for 8 hours at the temperatures 1350°C–1500°C. The phase composition of sintered ceramics was examined by means of X-ray diffraction analysis (XRD) using CuKα - radiation (Model PW 1700, Philips, Eindhoven, The Netherlands). Microstructural analysis of the ceramic samples was performed by means of scanning electron microscopy (JEOL, JSM 5800, Tokyo, Japan) using energy dispersive X-ray spectroscopy (EDX) and the LINK software package (ISIS 3000, Oxford Instruments, Bucks, UK). Room-temperature dielectric properties (ε and tan δ) were studied with Solartron 1260 A Impedance Analyzer (Solartron Analytical, UK) whereas low-temperature behavior was evaluated with Agilent E4980 Precision LCR Meter (Agilent Technologies Inc., USA) in the temperature interval of 2.5–300 K utilizing a home-made dielectric measurements probe coupled with the Physical Property Measurement System (Quantum Design, USA). The dielectric characteristics of the materials (ε and Q) at frequencies around 10 GHz were examined using a cavity reflection method and the sleeve resonator technique with the Network Analyser PNA-L Agilent N5230A (Agilent Technologies Inc., USA).

3. Results and Discussion

3.1. $Ba_9M^{2+}Nb_{14}O_{45}$ (M^{2+} = Co, Mg, Zn)

According to the XRD and SEM microstructural analysis, all of the studied materials with the compositions $Ba_9M^{2+}Nb_{14}O_{45}$ exhibit the presence of nearly single-phase TTB compound [7]. Within the radio-frequency (RF) region all of the studied 9:1:7 TTB phases demonstrate high values of dielectric permittivity ranging from $\varepsilon = 800$ to $\varepsilon = 1300$ (Table). At a fixed frequency, the permittivity magnitudes slightly increase with the increasing ionic radii of M^{2+} in the range Co-Mg-Zn (Table, Fig. 1). With increasing measurement frequency, all of the TTB compounds demonstrate strong frequency dispersion of permittivity (Table, Fig. 1). The observed dispersion is again stronger in the TTB compounds containing larger

Table 1
Room temperature dielectric parameters of $Ba_9M^{2+}Nb_{14}O_{45}$ ceramics

M^{2+}	ε (1 kHz)	tan δ (1 kHz)	ε (1 MHz)	tan δ (1 MHz)	ε (10 GHz)	tan δ (10 GHz)
Co	850	$3.0 \cdot 10^{-3}$	800	$3.8 \cdot 10^{-2}$	290	0.2
Mg	1100	$6.5 \cdot 10^{-4}$	1000	$2.0 \cdot 10^{-2}$	320	0.17
Zn	1300	$2.5 \cdot 10^{-3}$	1100	0.12	NA	NA

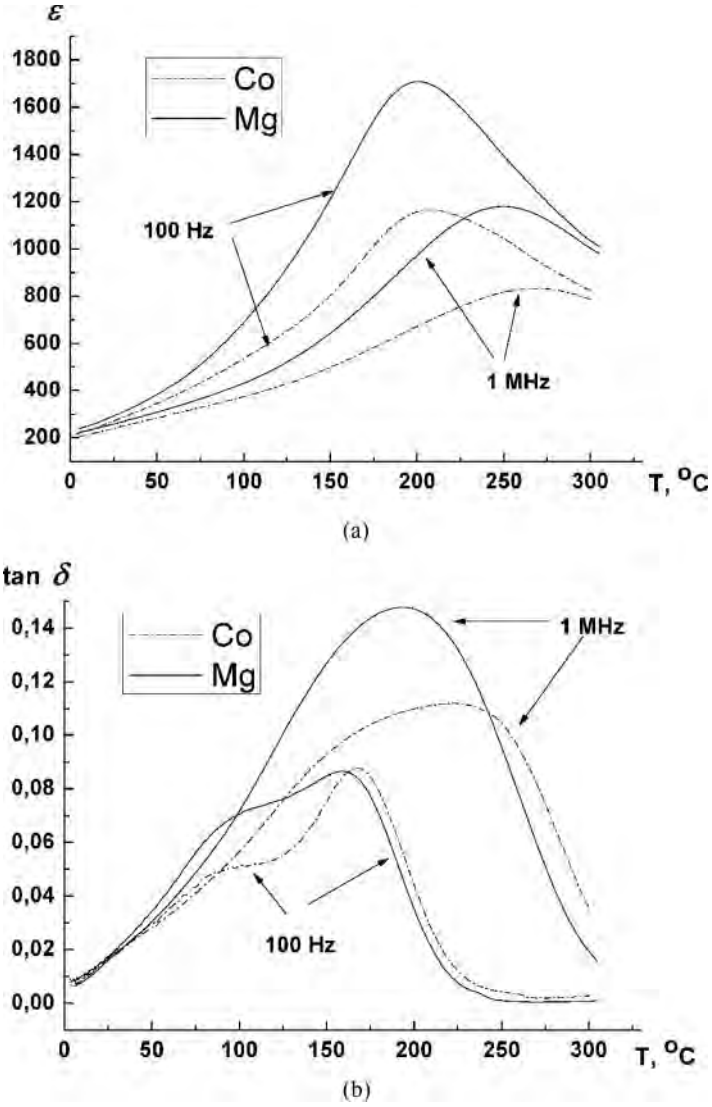

Figure 1. Temperature dependencies of the permittivity (a) and dielectric loss (b) of sintered $Ba_9M^{2+}Nb_{14}O_{45}$ (M^{2+} = Co, Mg) measured in the conventional frequency range.

cation M^{2+}, and is the most pronounced in the case of $Ba_9ZnNb_{14}O_{45}$. Low-temperature dielectric spectra of $Ba_9M^{2+}Nb_{14}O_{45}$ (Fig. 1) show a typical relaxor behavior of all studied TTB compounds [7]. The broad maxima on the dependencies of ε (T) and tan δ (T) have been found around 200–250 K and 100–200 K respectively in the case of M^{2+} = Co and Mg (Fig. 1), and at slightly higher temperatures in the case of M^{2+} = Zn [7]. At a fixed frequency, the temperatures corresponding to the maxima of ε and tan δ (T_M) increase with increasing ionic radii of M^{2+} (Fig. 1). In general, the dielectric spectra of $Ba_9M^{2+}Nb_{14}O_{45}$ indicate a broad distribution of the relaxation times denoting a high structural disorder of the studied TTB compounds [8]. In our opinion, this is likely due to the increasing degree of cation disorder in the TTB crystal lattice. This disorder may appear because of significant difference in the sizes of cations residing equal crystallographic sites.

When measurement frequencies are higher 10^6 Hz, the strongest fall of the permittivity magnitude of $Ba_9M^{2+}Nb_{14}O_{45}$ is observed (Table). As a consequence, within the microwave region, the permittivities of all studied compounds are around $\varepsilon = 300$ (Table), and exhibit weaker dependence on the size of M^{2+} comparing with the RF region. Over the entire studied frequency range (10^3–10^{10} Hz) the dispersion of permittivity is accompanied by a continuous rise of dielectric loss (Table). At microwaves, similarly to the permittivity, the room temperature dielectric loss have rather weak dependence on the M^{2+} species reaching values of tan $\delta = 1$–$2\cdot10^{-1}$. These values are indicative enough for understanding the observed drastic fall of the $Q\cdot f$ product of the materials based on high-Q perovskites which contain even a slight concentration of 9:1:7 TTB. Below, we will discuss this effect in more details.

3.2. Perovskite – TTB Composite Materials

Previously, we have shown that the 9:1:7 TTB compounds always form in the ceramics based on Ba-deficient perovskites $Ba(M^{2+}{}_{1/3}Nb_{2/3})O_3$ (M = Co, Zn, Mg) [6]. Out of the homogeneity ranges, any decrease in the Ba concentration results in the increasing amount of the corresponding TTB phase which is accompanied by a further suppression of the product Q·f (Fig. 2a). It should be noted that all of the sintered TTB phases exhibit low melting temperature of around 1400°C–1450°C, which is comparable with the sintering temperature of corresponding perovskites [6, 7]. Therefore, the TTB acts as a liquid phase

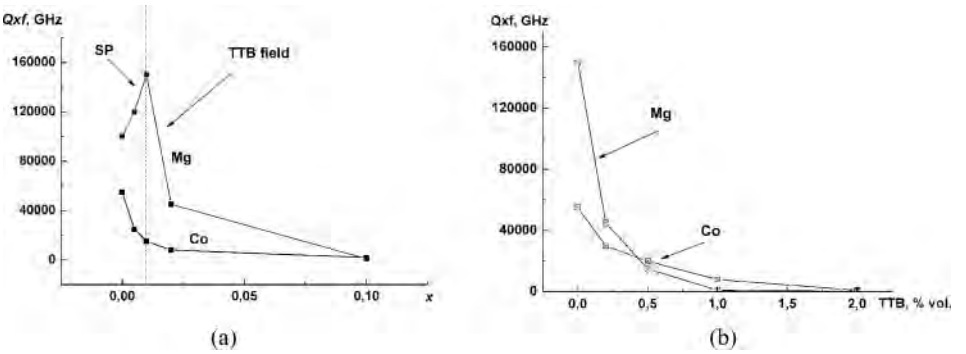

Figure 2. Product Q·f of $Ba_{1-x}(M^{2+}{}_{1/3}Nb_{2/3})O_{3-x}$ (M^{2+} = Co, Mg) materials measured at the frequency: f ∼ 10 GHz as a function of (a) Ba content and (b) volume concentration of the TTB phase in $Ba(M^{2+}{}_{1/3}Nb_{2/3})O_3$-TTB composite materials.

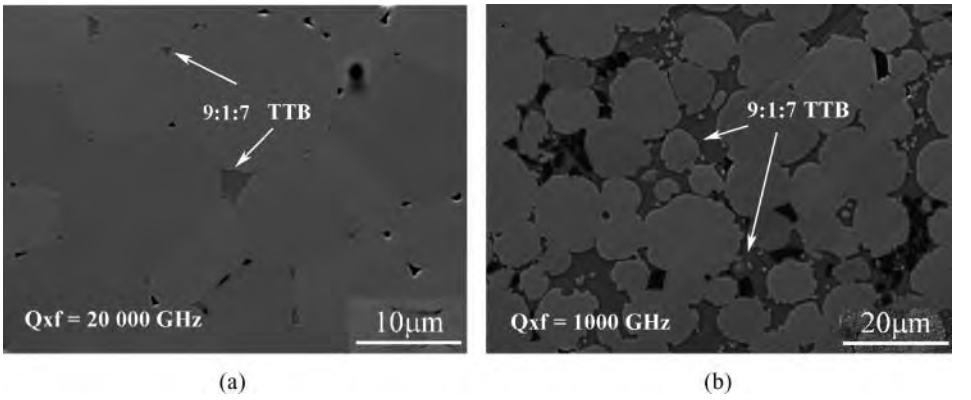

Figure 3. SEM microphotographs of the polished surface of the $Ba(Co_{1/3}Nb_{2/3})O_3$-TTB composite materials. TTB - $Ba_9M^{2+}Nb_{14}O_{45}$.

during the sintering of Ba-deficient perovskite, and is uniformly distributed between the grains of perovskite matrix (Fig. 3). Apparently, the intentionally composed materials based on a perovskite and corresponding TTB compound should demonstrate a persistent decrease in the product Q·f with increasing amount of a TTB phase. This is clearly seen on the Fig. 2b. Deriving from the microwave dielectric data collected from different TTB compounds, and corresponding perovskites, one can easily calculate the variation of the Q-factor in the composite materials as a function of the TTB volume fraction (Fig. 4). For this purpose, we used Maxwell-Garnet (1) and Lichtenecker's logarithmic law (2) due to their simplicity and good visibility [9, 10].

$$\varepsilon_{\text{eff}} = \frac{2\varepsilon_{\text{m}} + \varepsilon_{\text{i}} + 2\nu(\varepsilon_{\text{i}} - \varepsilon_{\text{m}})}{2\varepsilon_{\text{m}} + \varepsilon_{\text{i}} - \nu(\varepsilon_{\text{i}} - \varepsilon_{\text{m}})}\varepsilon_{\text{m}} \tag{1}$$

$$\ln(\varepsilon_{\text{eff}}) = (1 - \nu)\ln(\varepsilon_{\text{m}}) + \nu\ln(\varepsilon_{\text{i}}) \tag{2}$$

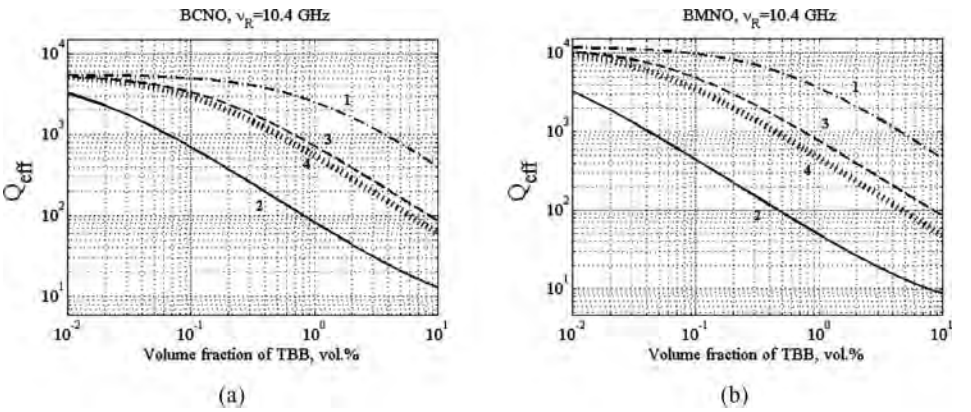

Figure 4. Simulation graphs for the dependence of the effective quality factor (Q_{eff}) at 10.4 GHz on the volume fractions of the TTB in $Ba(Co_{1/3}Nb_{2/3})O_3$ (a) and $Ba(Mg_{1/3}Nb_{2/3})O_3$-(b). 1 and 2- serial and parallel Wiener bounds respectively, 3 - Maxwell-Garnet mixing law, and 4- Lichtenecker's logarithmic law.

The results of the calculation are presented on the Fig. 4 for $Ba(M^{2+}{}_{1/3}Nb_{2/3})O_3$ –TTB composite (M^{2+} = Co and Mg). In both equation, ε_{eff} stands for the effective complex dielectric function of composite, ε_m – the complex dielectric function of host (matrix), ε_i - the complex dielectric function of TTB inclusions, and ν - volume fraction of TTB inclusions. The quality factors calculated according (1 and 2) for ε_i values corresponding to the frequency 10.4 GHz are shown in Fig 5 along with Wiener bounds. The host quality factors of BMN and BCN perovskites were assumed to be equal to 10^4 and $5{\cdot}10^3$ GHz respectively [5, 6]. The corresponding permittivity was set to the typically reported values. In the range of practical interest ($\nu < 5\%$), the dependence of Q_{eff} on ν is close to linear one in the logarithmic coordinates. Analysis of the presented simulations denotes their good correspondence with the experimentally measured data collected from the composite ceramics containing $Ba(M^{2+}{}_{1/3}Nb_{2/3})O_3$ and the TTB phase.

4. Conclusions

For the first time, the dielectric properties of the 9:1:7 TTB phases $Ba_9M^{2+}Nb_{14}O_{45}$ (M = Co, Mg, Zn) which form in Ba-deficient high-*Q* perovskite niobates $Ba(M^{2+}{}_{1/3}Nb_{2/3})O_3$ have been measured over the wide frequency range. We have shown that the dielectric relaxation found in $Ba_9M^{2+}Nb_{14}O_{45}$ is mainly responsible for their high dielectric loss in the microwave region. As a consequence, even a scarce amount of the TTB phase in the composite ceramics based on the high-*Q* perovskites $Ba(M^{2+}{}_{1/3}Nb_{2/3})O_3$ leads to significant degradation of the *Q*-factor that has been demonstrated by a simple simulation, and proved experimentally.

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